O-Functionalization of a Cobalt Carbonyl Generates a Terminal Cobalt Carbyne

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O-Functionalization of a Cobalt Carbonyl Generates a Terminal Cobalt Carbyne

Meaghan M. Deegan[a] and Jonas C. Peters*[a]

Despite efforts toward extending multiple bonding motifs to late metal systems, examples of late transition metal carbynes remain scarce. Herein, we describe the synthesis of a series of L₃Co(CO) complexes supported by a trisphosphine ligand framework, with the most reduced of these complexes being amenable to O-functionalization. This transformation provides access to the second reported example of a terminal Co-carbyne complex, in this case stabilized in a pseudotetrahedral geometry (i.e., L₃Co≡C-OSiR₃). Its geometry makes its electronic structure suitable for comparison to structurally-related examples of terminal Co-imido and oxo species.

One area of longstanding interest among synthetic inorganic and organometallic chemists is the study of species with metal-to-ligand multiple bonds (M=E, M≡E),[1] which serve as key intermediates in a variety of important synthetic and biological processes.[2] In recent years, there has been significant effort to extend these bonding motifs to late metal systems; relative to the mid-transition elements in groups 5 through 8, reports of late, and especially first row, metal systems that support strong, metal-ligand multiple bonds are less common, with reports of metal-to-ligand triple bonds (M≡E) almost exclusively limited to metal imidos.[3,4] For Co specifically, isolable examples of oxo[5,6] and carbyne[7,8,9] complexes having been reported only very recently; spectroscopic characterization of a terminal Co≡N species has also been reported.[10] Moving to the heavier group 9 elements, reports of Rh[11] and Ir[12] carbynes are similarly scarce (Figure 1A).

With this in mind, we became interested in targeting a pseudotetrahedral Co-carbyne complex for comparison to structurally-related Co-imido species[4d,13] and a recently reported Co-oxo complex[5] (Figure 1B). A substantial barrier to accessing carbynes beyond group 8 is the lack of synthetic
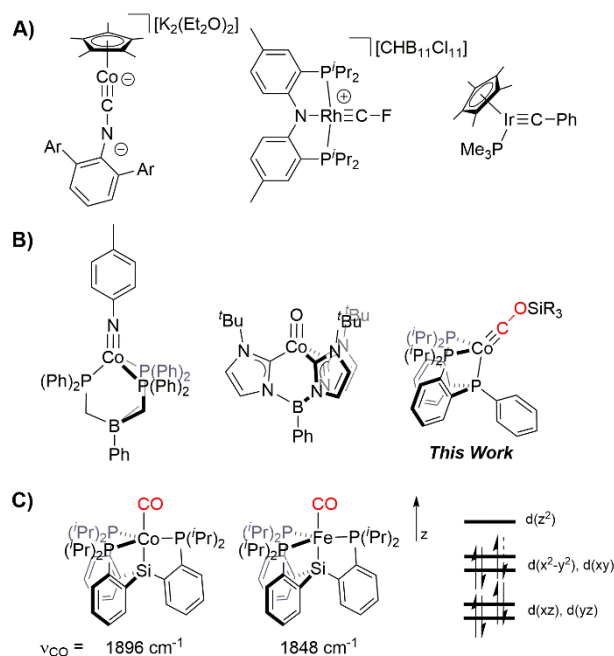

Fig. 1 A) Examples of isolable terminal carbyne complexes of group 9 metals.[7,11b,12] B) Representative examples of Co complexes stabilized in a pseudotetrahedral coordination environment.[3d,5] C) Comparison of CO activation at isostructural Co[I] and Fe[I] complexes.[15a,16] For both species, orbitals of d-parentage are shown to the right; the d(xz), d(yz) are of appropriate symmetry for π-backdonation to CO orbitals and are fully populated. The additional electron for the Co complex is located in the xy plane (indicated by the dashed half-arrow).

strategies that are easily translated to late metal systems. One intriguing approach to carbyne generation that has seen successful application in groups 5 through 8 is via the reductive functionalization of metal-ligated CO or CN ligands (i.e. [M-C≡O]¹⁻ + R⁺ → M≡C-OR; [M-C≡N]¹⁻ + 2 R⁺ → [M≡C-NR₂]⁺).[14,15] A challenge in translating this approach to a Co-system is overcoming its comparatively weak π-basicity, a byproduct of its enhanced electronegativity and contracted d-orbitals relative to earlier metal systems where this strategy has been successfully applied.

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For instance, comparing isostructural $[P_3^{Si}]Fe(CO)$ and $[P_3^{Si}]Co(CO)$, both with fully-populated orbitals of appropriate symmetry for π-backdonation into the CO ligand, moving from Fe to Co diminishes CO activation by ~50 cm^{-1} (Figure 1C).[15a,16] We postulated that moving to a sufficiently reducing supporting ligand might afford access to productive CO-functionalization to generate a rare example of a group 9 metal carbyne.

Building upon recent work from our group,[17] we targeted the use of a trisphosphine (P_2^P = PhP(o-$^iPr_2PC_6H_4$)$_2$) ligand. Initial access to the chemistry of $[(P_2^P)Co]$ was provided by *in situ* ligation of CoBr$_2$ with P_2^P in THF, followed by one-electron reduction with Na naphthalenide to yield dark red (P_2^P)CoBr **1** (Scheme 1; 71% yield). In solution, the paramagnetically-shifted ^1H NMR spectrum and magnetic moment (2.7μ_B; Evans Method) of **1** are consistent with a triplet ground state expected for a pseudotetrahedral Co^I complex. The crystal structure of **1** reveals a geometry that can be qualitatively described as lying between tetrahedral and trigonal pyramidal. In a quantitative sense, the geometric parameter τ_4, as described by Holland,[18] distinguishes between these limiting geometries, with a calculated τ_4 of 0.49 for **1**.

Complex **1** is a suitable precursor to monocarbonyl chemistry in this system; addition of an atmosphere of CO to a benzene solution of **1** resulted in the rapid formation of (P_2^P)CoBr(CO) **2** (Scheme 1; 95% yield). Diamagnetic **2** is generated as a 6:1 mixture of isomers in solution, as judged by NMR spectroscopy. In the solid state, **2** crystallizes with the CO ligand preferentially occupying the axial position of a distorted trigonal bipyramidal structure (τ_5 = 0.63[19]) opposite the central phosphine of the tris(phosphine) ligand.[20] The Co-ligated CO of **2** exhibits a diagnostic stretch at 1928 cm^{-1} (^{13}CO: 1884 cm^{-1}).

Reduction of **2** by addition of one equivalent of Na naphthalenide produces orange-red, zerovalent P_2^PCo(CO) **3**
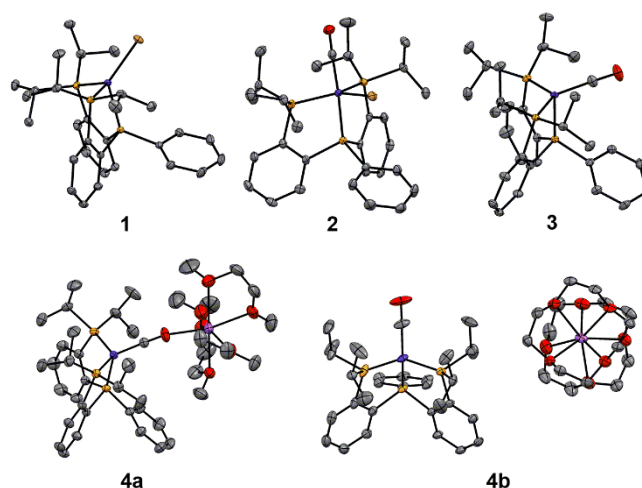

Fig. 2 Crystal structures of Co complexes with ellipsoids shown at 50% probability. Hydrogen atoms, solvent molecules, and disorder are omitted for clarity.

(Scheme 1; 81% yield).[21] Spectroscopic data for this transformation shows a shift in the CO stretch to 1866 cm^{-1} (^{13}CO: 1824 cm^{-1}), and the concomitant appearance of a pseudo-axial EPR signal. In the solid state, **3** adopts a distorted trigonal pyramidal geometry (τ_4 = 0.82), with the CO ligand deviating toward coplanarity with Co and the two P^{iPr} ligands; a similarly distorted structure was obtained upon DFT-optimization (τ_4 = 0.87; see SI).[22,23]

A further reduction step proved accessible by stirring **2** over an excess of Na metal, generating the anionic Co(-1) complex, $[P_2^PCo(CO)][Na(solv)_x]$ **4a**; this species could also be isolated as its crown-encapsulated Na salt $[P_2^PCo(CO)][Na(12$-crown-$4)_2]$ **4b**. To our knowledge, among reported Co complexes, **4b** promotes the highest degree of terminal CO activation, with the CO stretch observed in the IR spectrum of Na-capped **4a** at 1731 cm^{-1} (**4a**-^{13}CO: ν_{CO} = 1691 cm^{-1}), shifting to 1752 cm^{-1} in the crown-ether encapsulated Na salt **4b**. Like **1**, both **4a** and **4b** adopt a geometry lying between tetrahedral and trigonal pyramidal (τ_4 = 0.49), with strong π-backdonation into the ligands apparent from short Co-P distances (**4b**: 2.0838(8), 2.1191(8), 2.1304(7) Å vs. **3**: 2.1344(6), 2.1769(5), 2.1922(5) Å) and a contracted Co-C distance (**4b**: 1.733(3) Å vs. **3: 1.752(2)** Å), with corresponding elongation of the C-O bond (**4b**: 1.177(4) Å vs. **3**: 1.161(3) Å).[24]

Anionic **4a** exhibits a degree of CO activation comparable to the reduced Fe species $[P_3^{Si}Fe(CO)][Na(THF)_3]$ (Figure 1A; ν(CO) = 1717 cm^{-1}) and, for the Na-capped structure, similar M-C (1.732(8) Å) and C-O (1.188(3) Å) bond distances.[15a] $[P_3^{Si}Fe(CO)][Na(THF)_3]$ was successfully used to demonstrate CO-to-carbyne conversion via silylation, setting the stage to explore a related transformation with **4a** to afford a terminal cobalt-carbyne. To our satisfaction, treating **4a**[25] with the sterically-hindered silyl-triflate electrophiles $^iPr_3Si$- or $^tBuPh_2SiOTf$ promoted the clean generation of a new diamagnetic product (**5a** and **5b**, respectively) in both cases (>90% yield; Figure 3), void of the terminal Co-CO stretch observed in the IR spectrum of the precursor **4a**. In the $^iPr_3SiOTf$ case, the assignment of **5a** as the product of O-functionalization of **4a** was corroborated by preparation of its ^{13}CO-labeled
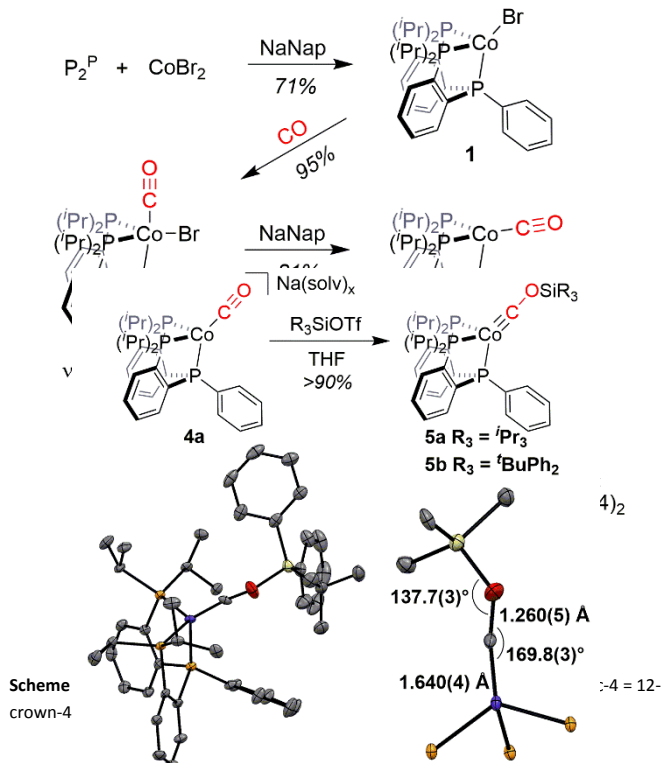

Scheme crown-4

Fig 3 Reactivity of 4a with silyl triflate electrophiles to generate carbyne 5 (top). The crystal structure of shown 5b is shown with ellipsoids depicted at 50% probability; hydrogen atoms and disorder are omitted for clarity (bottom left). A truncated structure of 5b is depicted highlighting the bonding in the carbyne ligand (bottom right).

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analog **5a-^{13}COSi^{i}Pr$_3$**. The solution IR difference spectrum of **5a** and **5a-^{13}COSi^{i}Pr$_3$** allowed for the identification of the C-O stretch in the fingerprint region of the spectrum at 1387 cm^{-1} (^{13}CO: 1347 cm^{-1}), higher than typically observed, for example, in silyl ethers (~1250 cm^{-1}), but clearly lower than bona fide C=O double bonds (>1650 cm^{-1}), consistent with the formation of a species that retains little C-O multiple bond character.[26] The ^{13}C NMR carbonyl resonance shifts from 227.2 ppm in **4a-^{13}CO** to 229.8 ppm in **5a-^{13}COSi^{i}Pr$_3$**.

Solid-state characterization of the ^{t}BuPh$_2$Si-functionalized complex **5b** confirmed its assignment as a terminal carbyne complex (Figure 3). Substantial contraction in the Co-C bond

electronic structures of these compounds, the key distinguishing interactions are the Co-ligand π interactions. Combined, the spectroscopic observations and the computational MO picture are consistent with strong M-to-L multiple bonding, as is the case for the Co(O) and Co(NAd) compounds, and distinct from the anionic CO complex. However, for the Co(O) and Co(NAd) complexes, predominant localization of the vacant π* orbitals on Co, is consistent with π bonding interactions from the π-donating oxo and imido ligands to a relatively oxidized Co center. The polarity of these interactions is inverted in the carbyne complex **5b**, with π-donation from filled Co-localized orbitals into a strongly
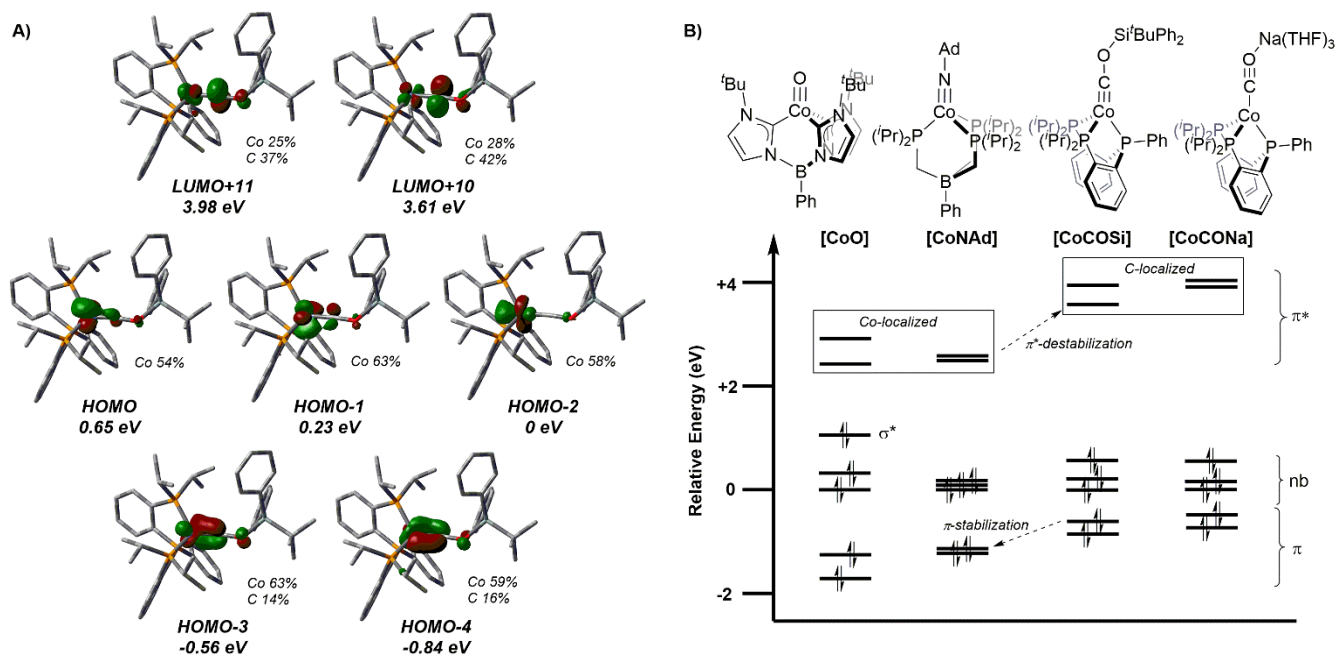

Fig 4 A) Select MOs derived from the DFT-optimized structure of **5b**. Orbital energies are listed relative to the HOMO-2 orbital in eV. Calculated contribution of Co d-orbitals for each MO are noted. C p-orbital contributions are noted where ≥ 10%. Lobal representations are shown with 0.07 isocontours. B) Comparison of MO splitting diagrams for pseudotetrahedral Co complexes obtained computationally (M06-L functional: def2tzvp (Co), def2svp (all other atoms)).[5,26] Relative orbital energies are referenced to the lowest energy Co-localized non-bonding orbital, in each case the HOMO-2 (see the Supporting Information for additional computational details).

distance (1.640(4) Å) and a corresponding elongation of the C-O distance (1.260(5) Å) occurs upon O-silylation from **4a** to **5b**. Slight bending is also observed in the Co-C-O angle (169.8(3)°) of **5b**, with substantial bending at the C-O-Si bond (137.7(3)°). Collectively, the structural and spectroscopic observations for complex **5** track closely with those made for similar CO-derived carbyne complexes of Fe,[15a,b] as well as other reported examples of Fischer-type carbyne complexes of Fe[15c,d,27] and the single, structurally characterized terminal Co-carbyne complex.[7]

In reports of heteroatom-substituted carbynes of Fe (and most recently, Co), we and others have argued that complexes akin to **5** can be described with a formally low-valent metal center π-backdonating into a strongly accepting and hence Fischer-type carbyne ligand.[15a,7] In a limiting sense, this suggests that the electronic structure of **5** relates more closely to that of its precursor **4** than structurally-related Co(III) imido or oxo species. This idea is partially borne out in a computational comparison of a series of pseudotetrahedral Co complexes, including previously reported Co(O)[5] and Co(NAd)[28] species, as well as compounds **4a** and **5b** (Figure 4). In considering the

accepting carbyne ligand, akin to backbonding in the reduced carbonyl complex **4a**. While these comparisons suggest electronic structure perturbations across this series of compounds, simple consideration of formal oxidation state assignments fails to underscore the role of strong covalency required for the stabilization of these species.

To conclude, we have prepared a series of Co(CO) complexes, which, in the most reduced state, support a remarkable degree of terminal CO activation. This highly-reduced state is reactive towards O-functionalization with a silyl triflate electrophile to generate a very rare example of a terminal Co-carbyne complex. Like related iron and cobalt species, experimental and computational evidence support its assignment as a carbyne, with strong π-backdonation from Co to the carbyne ligand.

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Conflicts of interest

There are no conflicts to declare.

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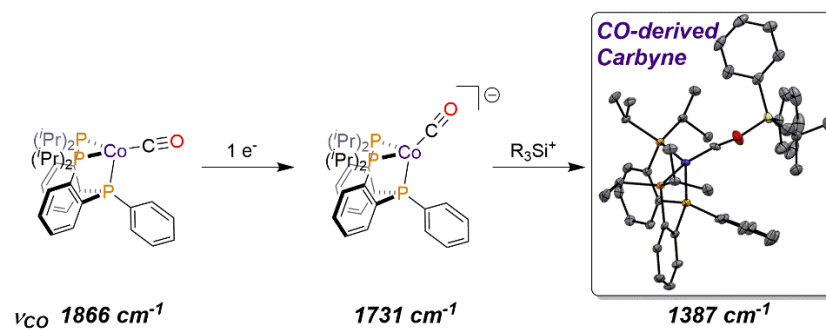
We describe the synthesis of a series of terminally-bound Co-carbonyl complexes, with the most reduced state amenable to O-functionalization to generate a rare example of a late transition metal carbyne.